Supporting Information

Construction of dendritic Janus nanomotors with H_2O_2 and NIR light dual-propulsion via Pickering emulsion

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SUPPORTING METHODS

Materials. Tetraethyl orthosilicate (TEOS, ≥ 98%), triethanolamine (TEA, ≥ 99%), cetyltrimethylammonium tosylate (CTA·Tos, ≥ 98%), 3-aminopropyltriethoxysilane (APTES, 98%), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM] OTF, ≥ 95%), concentrated hydrochloric acid (HCl, 37%), hexachloroplatinic (IV) acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, ≥ 99%), trichloromethane ($CHCl_3$), Copper (II) Chloride Dihydrate ($CuCl_2 \cdot 2H_2O$), trisodium citrate dihydrate ($Na_3Cit \cdot 2H_2O$), Sodium sulfide ($Na_2S \cdot 9H_2O$), sodium borohydride ($NaBH_4$), paraffin wax, sodium dodecylsulfate (SDS), anhydrous ethanol were purchased from Beihua Fine Chemicals. Ultrapure water with a resistivity higher than 18.2 MΩ·cm was used in all experiments and was obtained from a three-stage Millipore Mill-Q Plus 185 purification system (Academic).

Synthesis of dendritic porous silica nanoparticles (DPSNs). Monodispersed DPSNs were synthesized using CTA·Tos and [BMIM] OTF as surfactants, TEA as a mineralizing agent, water as a solvent and TEOS as a silica source. A typical synthesis of DPSNs with the diameter of 250 nm was performed as follows: a mixture of CTA·Tos (0.96 g), TEA (0.105 g), [BMIM] OTF (300 mg) and water (50 mL) was stirred at 80 °C for 1 h, and then TEOS (7.8 mL) was quickly added into the surfactant solution. The mixture was stirred with a speed of 1000 rpm at 80 °C for another 2 h. The formed DPSNs were centrifuged and washed with ethanol and water. Then, the CTA·Tos was removed from particles by template extraction. The as-prepared DPSNs (1.0 g) were added into ethanolic HCl (concentrated HCl (15 mL) in ethanol (100 mL) and sonicated for 2 h. The suspension was stirred at 70 °C for 24 h. The extraction procedure was repeated twice to remove the surfactant efficiently. Finally, the precipitates were centrifuged, washed with ethanol, and dried in a vacuum oven at 60 °C for 24 h.

Synthesis of citrate-stabilized Pt nanoparticles. Citrate-stabilized Pt NPs were synthesized as reported previously. Typically, 26 mL of sodium citrate aqueous solution (2.8 mM) was added to 50 mL of $H_2PtCl_6 \cdot 6H_2O$ aqueous solution (0.4 mM) at room temperature. The mixture was stirred to mix well, and then 5 mL of $NaBH_4$ (12 mM) was added dropwise with vigorous stirring (stirring bar with a size of 4 cm, 400 rpm). The pale-yellow solution turned dark-brown in 5 min and was kept stirring for 2 h. The as-prepared Pt colloids should be stored in a refrigerator at 4 °C for further use. The concentration of Pt NPs is calculated to be 0.247 mmol L^{-1}.

Synthesis of citrate-capped copper sulfide nanoparticles. Negatively charged CuS NPs were synthesized according to the previous report. 10 mL of $CuCl_2$ solution (0.85 mg mL^{-1} in water) and 10 mL of sodium citrate (1.0 mg mL^{-1}) were added into 30 mL of water followed by constant stirring for 30 min at room temperature. After that, 50 μL of aqueous solution of Na_2S (60.54 mg in 250 μL) was added to the mixture and stirred for another 5 min before transferring to a 90 °C water bath. After 15 min, the solution was cooled down with ice, finally forming CuS NPs suspension with green color. The as-prepared CuS colloids should be stored in a refrigerator at 4 °C for further use. The concentration of CuS NPs is calculated to be 0.997 mmol L^{-1}.

Aminopropyl-functionalization of DPSNs. The functionalization of aminopropyl groups on the surface of DPSNs was carried out by the post-grafting method. In a typical procedure, 1.0 g of DPSNs were dispersed in 80 mL of anhydrous ethanol in a single-round bottom flask, and the mixture was treated by ultrasonic dispersion at an ultrasonic power of 300 W for 30 min. After the mixture was stirred at 80 °C for 30 min, 1.0 mL of APTES was added and continued to stir at 80 °C for 12 h. The aminopropyl-functionalized DPSNs (DPSNs-NH_2) were obtained by washing with ethanol three times and dispersed in ethanol to form suspensions for further use.

Morphology and structure characterization. For transmission electron microscopy (TEM) observations, powder samples were added on carbon-coated copper grids and observed on a Hitachi HT-7700 transmission electron microscope at an acceleration voltage of 100 kV. Scanning electron microscopy (SEM) observations were carried out on a Hitachi S-8010 scanning electron microscope operated at 10 kV. Specimens were coated with a layer of gold with a size of 5 nm by ion sputtering before SEM observations. Nitrogen adsorption-desorption measurements were carried out on a QuadraSorb SI automated surface area and pore size analyzer. Before the measurement, the products were degassed at 120 ˚C for at least 6 h. Brunauer-Emmett-Teller (BET) specific surface areas were calculated by using adsorption data at a relative pressure range of P/P_0 range of 0.05-0.25. Pore size distributions were estimated from the adsorption branch of the isotherm using the Barrett, Joyner, and Halenda (BJH) method. Pore volumes were determined from the amounts of N_2 adsorbed at the single point of P/P_0=0.98. The zeta potentials of various nanoparticles were measured by using a Malvern Zetasizer Nano ZS90 equipped with a DTS1070 cell at room temperature. UV-vis absorption spectra in the wavelength range of 300–1100 nm were measured by with a Shimadzu UV1800 spectrophotometer.

SUPPORTING FIGURES

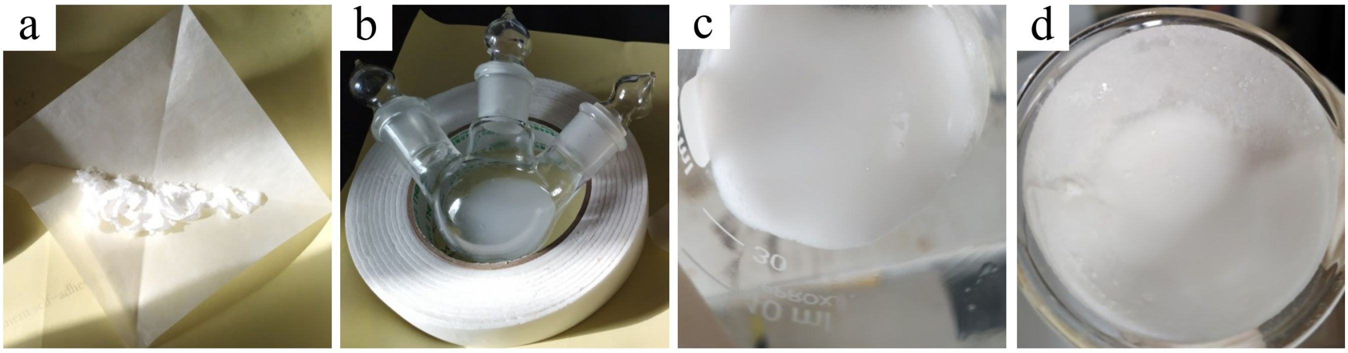
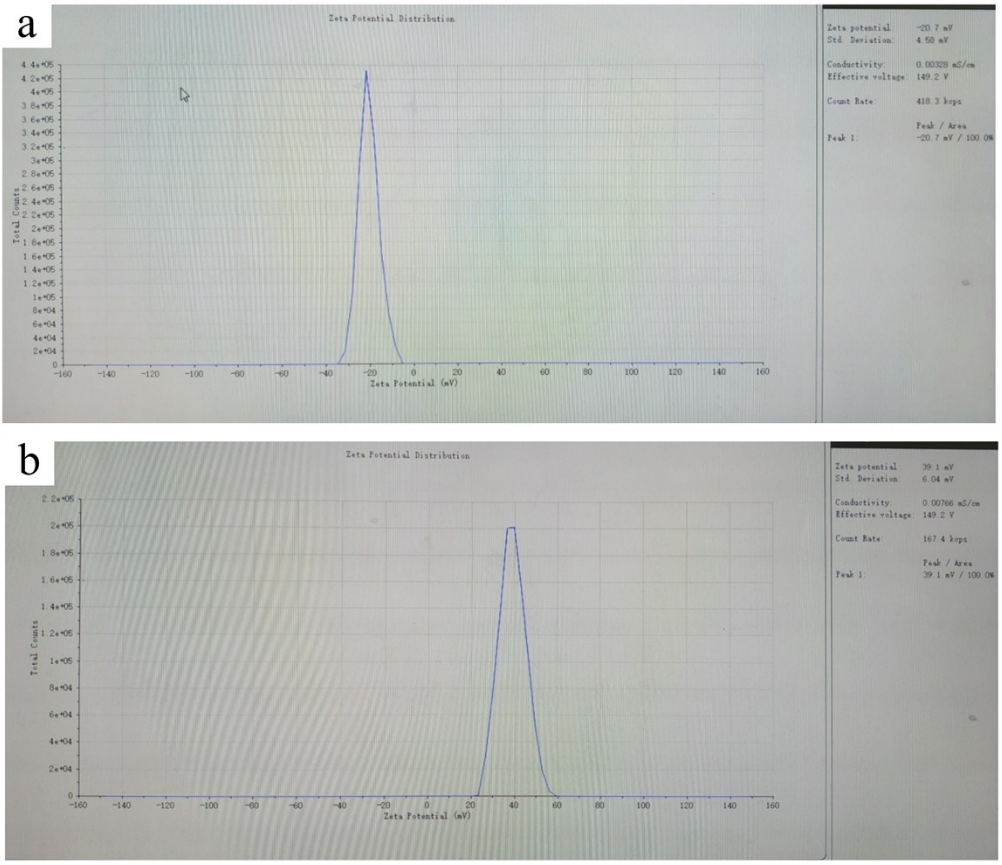


Figure S1. Digital images of (a) paraffin wax; (b) SDS and DPSNs-NH_2 suspension; (c) DPSN-NH_2-stabilized wax; (d) wax-DPSNs-NH_2 microparticles after filtration.



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Zeta potential:        -20.7 mV
Std. Deviation:        4.58 mV

Conductivity:          0.00328 mS/cm
Effective voltage:     149.2 V

Count Rate:            418.3 kcps

                       Peak / Area
Peak 1:                -20.7 mV / 100.0%
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Zeta potential:        39.1 mV
Std. Deviation:        6.04 mV

Conductivity:          0.00766 mS/cm
Effective voltage:     149.2 V

Count Rate:            167.4 kcps

                       Peak / Area
Peak 1:                39.1 mV / 100.0%
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Figure S2. (a-b)The zeta-potential of aminopropyl-modification DPSNs changed from -20.7 mV to +39.1 mV.

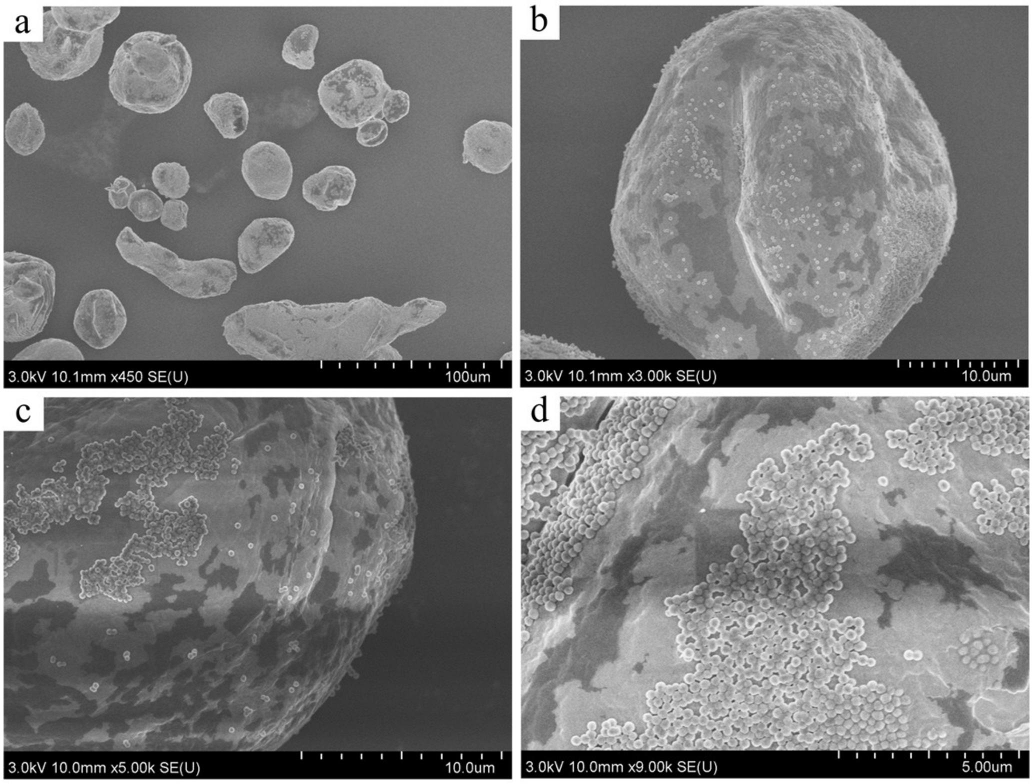

Figure S3. (a-d)TEM images of wax-DPSNs microparticles when watched with plenty of ethanol.

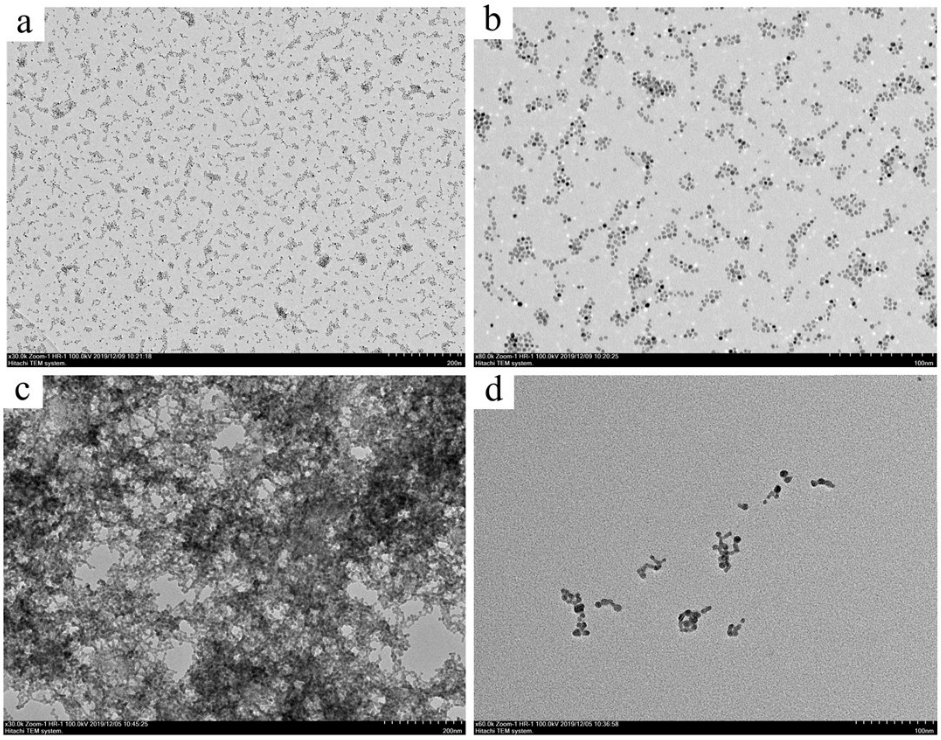

Figure S4. TEM images of (a-b) citrate-stabilized Pt NPs with particle size of 3.3 ± 0.6 nm; (c-d) citrate-stabilized CuS NPs with particle size of 7.8 ± 1.9 nm.

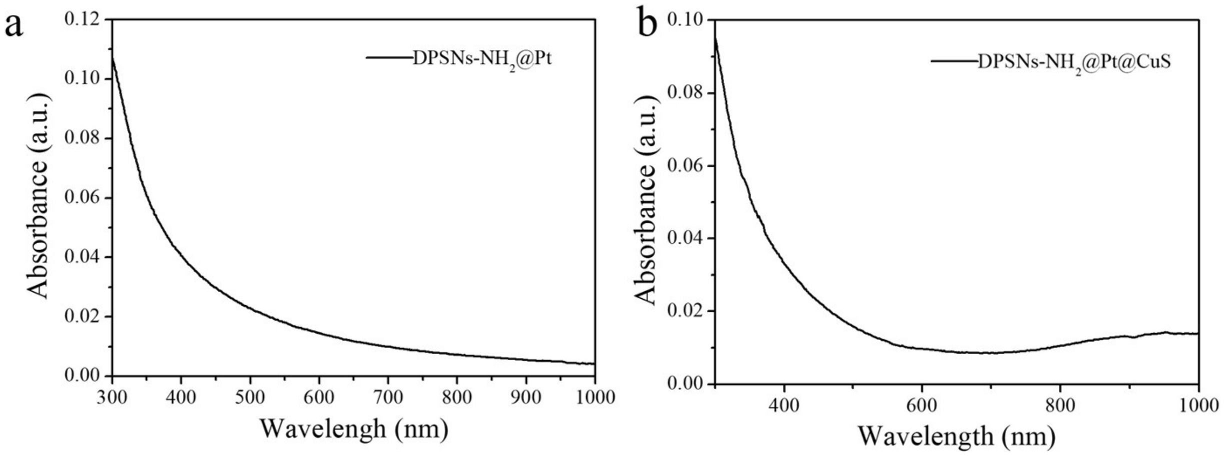

Figure S5. (a-b) UV–vis–NIR absorption spectra of DPSNs-NH$_2$@Pt NPs and DPSNs-NH$_2$@Pt@CuS NPs.

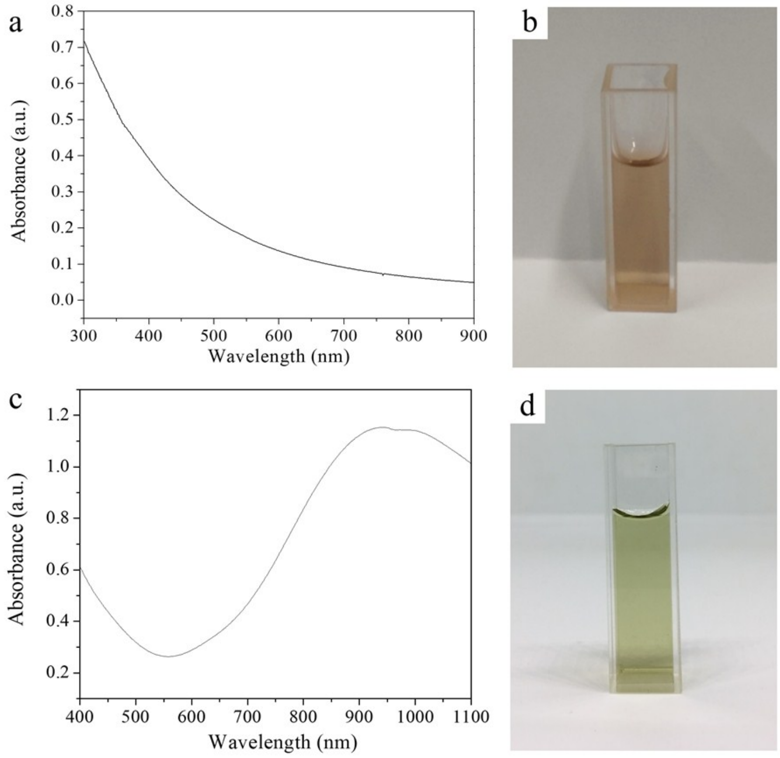

Figure S6. (a,c) UV–vis–NIR absorption spectra and (b,d) the corresponding digital images. (a-b) citrate-stabilized Pt NPs with particle size of 3.3 ± 0.6 nm and zeta-potential of -33.4 mV; (c-d) citrate-stabilized CuS NPs with particle size of 7.8 ± 1.9 nm and zeta-potential of -28.6 mV.